2-19-2008

The study of the effect of oxygen permeation resulting from adding a high barrier shrink film to a PET beer bottle

Jeffrey T. Spiwak

The Study of the Effect of Oxygen Permeation Resulting from Adding a High Barrier Shrink Film to a PET Beer Bottle

by

Jeffrey Spiwak

A Thesis Project

Submitted to the

Department of Packaging Science

College of Applied Science and Technology

In partial fulfillment of the requirements for the degree of

Master of Science

Rochester Institute of Technology
2008

Department of Packaging Science

College of Applied Science and Technology

Department of Packaging Science

College of Applied Science and Technology

Rochester Institute of Technology

Rochester, New York

CERTIFICATE of APPROVAL

M.S. DEGREE THESIS

The M.S. degree thesis of Jeffrey T. Spiwak

has been examined and approved

by the thesis committee as satisfactory

for the requirements for the

Master of Science Degree

Dr. Changfeng Ge	Changfeng Ge
Dr. Daniel Goodwin	Daniel Goodwin
Mike Gasser	Mike Gasser

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The Study of the Effect of Oxygen Permeation Resulting from Adding a High Barrier Shrink Film to a PET Beer Bottle.

ACKNOWLEDGMENTS

I would like to thank the members of my thesis committee: Dr. Changfeng Ge Professor Packaging Science and MET , Dr. Daniel Goodwin Professor of Packaging Science, and Mike Gasser VP of Packaging at High Falls Brewery. Special thanks to Dr. Changfeng Ge for taking the extra time out his personal schedule to meet with me on weekends at RIT to actively support my work and approach.

I would also like to thank the following people for their valuable time and support for this study: James Gross RIT Packaging Science Graduate Student for his support on our many ideas and collaborations; Erin M. Suedkamp from Curwood Films a division of Bemis for supplying all shrink material for this study; John Glass RIT MET Undergraduate Student for his lab support.

In addition to those who provided their direct support on this project, I would also like to thank all the program instructors and RIT staff for making this program a wonderful experience.

Most of all I would like to thank my amazing wife and my parents for their unwaivering support. None of this would have been possible without them.

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ABSTRACT

The purpose of this research was to investigate the effect of oxygen permeation from adding a high barrier shrink film to PET beer bottles at ambient temperature and humidity. The testing method used for this research is based off ASTM D 3985 "Standard Test Method for Oxygen Gas Transmission Rate through plastic film and sheeting using a coulmetric sensor." The test results indicated that there was statistical difference between the samples that were covered in barrier shrink film and those that were not covered. The results demonstrated that at ambient temperature and humidity, that there was significant improvement over plain PET structures.

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CHAPTER 1: INTRODUCTION

As most beer bottles are made from glass for its various reasons—absolute barrier, processing, pasteurization, robustness, rigid structure, along with traditional marketing and production capability—the industry is turning with steady growth in the areas of PET bottling research and development. During 2002 and 2003, sales of PET beer bottles increased by 20% to 30% in Europe, while growth in Russia had increased to 39% (Packaging Gateway, 2006). According to a study done by Zerdine and Steele (2005), world beer container demand for PET beer bottles had increased 10% overall throughout the global market in 2005. This equals 9.7 billion units sold globally.

Major breweries such as: Miller Brewery (USA), Carlton Brewery (Australia), Bass Breweries (UK), Heineken (Netherlands) and Kirin Breweries (Asia), have all utilized PET beer bottles in recent years. Although the growth in consumer acceptance of PET beer bottles has increased in the past 10 years, there are still challenges that face the industry with polymer bottling for such an oxidative product such as beer. The main issue is keeping the product from spoiling due to oxygen ingress through the plastic wall of the bottle.

The main focus of this thesis research will be examining the oxygen permeability of PET bottles, and how barrier shrink film can be used to slow down the steady state of oxygen transfer into the bottle and product. This research will examine how an outer shrink film reacts to oxygen permeation. In addition to adding increased barrier to bottles, this method of packaging may allow easier adaptability to an existing bottling line. The high barrier shrink film would be an additional line function that could be adapted to the bottling line after the pasteurization process and before case packing, to which each individual PET bottle would be barrier shrink wrapped.

Background

The performance of a successful package is gauged by it's utility, not only to the customer, and consumer, but also to the manufacturer. Performance of packaging is the key to its success in the market place, but while this is the primary focus, getting this done while meeting the operation efficiencies of the manufacturer is just as important. This thesis will focus on how oxygen ingress is effected by an added barrier shrink film applied to the outside of the bottle. This method of adding oxygen barrier to the product would be set-up as an end process that may be added to the end of the line for simplicity (Appendix C).

In recent years, there has been lots of research done on how to make PET beer bottles more stable against oxygen permeation. The plastics industry has been successful with developing bottle technologies that offer increased shelf life in beer without using glass. However, the down fall to these developments have been both cost of producing these plastic structures which outweigh their current demand. Although there is an increase in PET beer bottles overall within the market globally, the development of compatible polymer layers in cavity blow molding is a very complicated process. Attempts to overcome the problem of plastic bottles have often involved multi-layered bottles where one of the layers comprises of a polymer such as EVOH (ethylene vinyl alcohol copolymer), having superior passive resistance to oxygen permeation as compared to the bottle which is only PET.

There are however disadvantages to such approaches, including the following: (1) the bottles are no longer suitable for recycling and are more difficult to separate layering, (2) the bottles tend to delaminate at the PET / EVOH interfaces, although delamination may be some what diminished at an additional expense, (3) the difference in melting points and other physical properties of the mulit-layered structures cause numerous problems in bottle fabrication (Chen 2003).

Although current bottle manufactures face these issues, this is not the focus of the study. But rather, the focus will be the utility of using barrier shrink films, not as a substitute for multi-layered or coated structures, but as an additional component to the primary packaging. To use a barrier shrink film that can be printed, while still yielding barrier functionality to it.

The benefits to PET beer bottles have without question been realized: customization of molding images into the bottle wall, lighter structure decreases shipping and warehousing cost, and adapting plastic bottles to niche markets that are ideal for a light weight indestructible design—stadiums and concerts. These attributes of the PET bottle are the reasons behind industry interest in developing a bottle that has high oxygen barrier properties. Thus, the very reason of understanding whether or not there is any significance to adding a high barrier shrink film to a plain biaxially orientated PET bottle, to help aid in barrier performance against O_2 must be investigated.

Problem Statement

The success of PET beer bottle packaging in regards to oxygen permeation is determined by how much allowable oxygen enters through the bottle wall over time. Although multi-layered and special coated bottles have been developed in order to resolve this issue, these bottle manufacturing processes are complicated and expensive. This study of the effect of oxygen permeation resulting from adding a high barrier shrink film to a PET beer bottle is, therefore, necessary to understanding possible oxygen barrier alternatives that may help to ultimately reduce cost. However, this research will prove if in deed there is any oxygen barrier benefits to adding a high barrier shrink film to the outside of the bottle, which may ultimately have beneficial cost savings associated to the primary structure.

Objective of the Research

The objective of this thesis research is to determine whether there is any change in oxygen permeation to a PET beer bottle after adding a high barrier shrink film to it.

Thesis Statement

Adding a high barrier shrink film to PET beer bottle will reduce the overall oxygen permeation rate of the bottle.

Scope of the Research

The primary goal of this thesis research is to examine the oxygen permeation of a PET bottle through its PET wall structure in efforts to quantify oxygen transmission rates. In conjunction to understanding oxygen permeation through standard plain PET bottle material, this thesis will go further to understand how oxygen barrier shrink film will effect the plain PET bottle permeation rates of oxygen. This study did not examine the affects of desorption from the closure liner, permeation of the closure, or ingress due to the loss of seal integrity. Rather, this study focused on the absorption and desorption of oxygen into the wall of the bottle, with an added barrier enhanced shrink film.

The performance measure used to evaluate the bottles was oxygen transmission rate (OTR). The test schedules and procedures for OTR of the test specimens were based on the ASTM D 3985 "Standard Test Method for Oxygen Gas Transmission Rate through Plastic Film and Sheeting using a Coulometric Sensor." Details of test specimens and methods are provided in Chapter 3.

CHAPTER 2: LITERATURE REVIEW AND BACKGROUND THEORIES

Bottling manufactures have been experimenting with plastic technologies for years, but only in the last decade have significant technological advancements in the bottling industry become marketable (Huige 2002). Mainly issues concerning the decrease in flavor stability due to excessive amounts of oxygen entering the packaging structure limits plastic packaging. Because beer is extremely oxygen and light sensitive, it needs approximately 120 days of shelf life to accommodate the distribution chain (Zerdine and Steele, 2005).

Quasi-Steady-State -Permeation

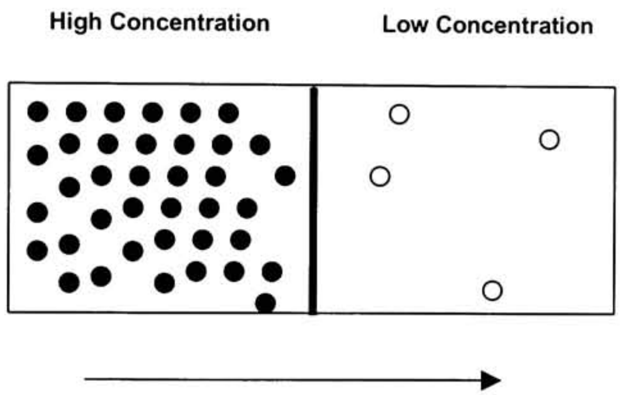
The focus of oxygen desorption through the bottle wall from the outside atmosphere into the package is what oxidizes beer, making it undesirable. This gas transfer is referred to quasi-steady-state permeation. Gas or vapor molecules move from the high-concentration side to the low concentration side. This is where O2 moves into the beer while CO2 and water vapor move out of the beer (Huige, 2002).

Figure 2-1 Quasi Steady State Permeation

Mulholland proved in using PET and PEN that the O_2 and CO_2 are co-dependent of each other, and have no effect while crossing paths in permeation. The rate at which this occurs depends on the barrier material or coatings being used for the packaging structure, along with thickness of material, and the atmospheric environment that the material is subjected to, as well as time. Thus the rate of O_2 permeation is not effected by CO_2 pressure or CO_2 volume in each bottle.

Quasi-Steady-State –Permeation is a factor of molecular diffusion. The Diffusion is the net movement of molecules, from a higher concentration to a driving force of diffusion is concentration gradient, which can be increased by higher temperature and higher relative humidity.

Figure 2-2 Net Flow of Diffusion



The bottle thickness is also very influential in permeation, as is also the surface area of the bottle. A larger structure that has more surface area and thinner wall thickness will yield a higher permeation rate at these thinner points. Most often the bottle wall in the center is the weakest point for 0_2 ingress and $C0_2$ loss. Bottle structures by design have a much thicker shoulder, neck and bottom due to the cavity forming process. This gives the bottle increased structural integrity against compression and stress, but also increases the barrier of the bottle in those particular areas of the bottle. This means the thinner center portion of the bottle—labeled section—is where most of the permeation happens (Yambrach 2007).

Figure 2-3 Different Thickness Points of the Bottle

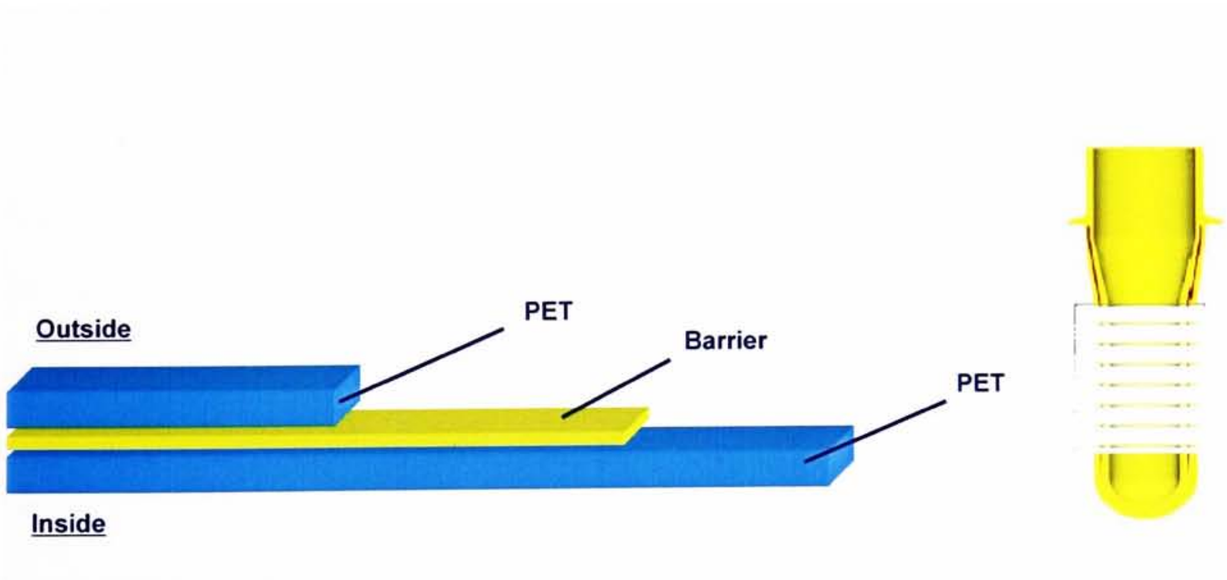
Multi-Layered & Barrier Coated Bottle Structures

The idea of the multi-layered structure was made in order to break up the steady-state of permeation flux. In order to do this, a proper barrier needs to be able to disrupt this mechanical transfer of gases. Because of this steady-state of oxygen transfer, many packaging technologies being used are multi-layer wall oxygen barrier structures. These technologies consist of co-extruded and tie layered and laminated processing that bonds the materials together in order to achieve certain characteristics. This can be done at the manufacturing level, or converter level. However, for bottling applications, the preforms of the bottle before injection blow-molding are formed in a multi-layer cavity structure, made with varying polymers. Many of these bottles using this method exist today, and are currently being tested for better improvement for longer shelf-life (staying fresh at the retail, consumer and storage environments).

Figure 2-4 Multi-Layered Structure

Currently, there are many multi-layered PET bottle structures that work well in the industry, particularly for beer applications. These structures normally consist of the following materials and layering: PET/EVOH/PET or PET/MXD6 polyamide/PET. Using EVOH barrier materials; tie layering is needed as this particular polymer is difficult to adhere to non- polar polyolefins and is relatively difficult to co-extrude or laminate. The PET is used on the outside of the structure, then a tie layer is used to adhere the PET to the barrier EVOH material, and this combination is used on the other half symmetrically—inside wall. Many times a moisture desiccant can be added to the tie layering of the structure to absorb the moisture to preserve the dryness of the EVOH—since the presence of water molecules decreases the oxygen barrier of this particular example of O_2 barrier.

Figure 2-5 PET/ Barrier Material/ PET Parison Structure



Unlike EVOH, polyamides, or MXD6 (specialty nylon grade) do not need tie layering because of its hygroscopic nature—polarity—but more importantly because of it's higher melt temperature. This means that the material can bond easily to other materials while at its melt temperature, and keep those bonds after cooling.

Although the permeation rates of these particular polymer combinations are both very low, they exhibit different reactions in testing. An EVOH structure depending on the thickness will generally yield ~ .007cc/ m2 day atm (Metric). The MXD6 polyamide will start higher at [.01cc/m2 day atm] but will stay more stable through it's product life on the shelf, and not peak out around 70-80% RH levels (Maul 2005). Over a period of time the barrier property of nylon will stay more constant while EVOH will begin to deteriorate.

The OTR of multi-layered beer bottles from the industry exhibit exceptionally high performance, on average .00306cc/package/ 24hrs atm. Ball Corp. Innovative Technology utilizes two different multi-layered pre-forms structures that are biaxially orientated with the multi-layered material sandwiched in the center. The two different multi-layered structures yield an OTR of .00378cc, and .00233cc/package/24hrs atm for their 12oz bottles.

Other barrier technologies include: oxygen scavenging wall coating and bottle crowns coatings, vacuum deposited silica oxide additives, vacuum deposited MET and plasma coating technology. These can be adhered to the outside and inside of the structure depending on the manufacturer's capabilities.

Figure 2-6 Barrier Coated Beer Bottles

Ball Inc. Plastic Innovation Presentation

Figure 2-6 shows Ball Corps barrier coating technologies, of both the Plasmax $Si0_x$ and their carbon coating technology in 12oz format. The Plasmax $Si0_x$ yields on average .00099cc/package/24hr atm, while their carbon coated is around .00076cc/package/24hr. atm. Another beer manufacture Kirin Beer uses inner plasma coating technology that yields on average .0003cc/package/24hr-atm.

Environmental Factors Influencing Permeation

Shelf-life of plastic beer bottles when filled with beer have many different working forces that play against it. High temperature and humidity have significant roles on how the steady-state gas transfer permeates through different structures. The following table shows the Oxygen Transmission Rate (OTR) of barrier materials when subjected to increased humidity and temperature. It shows that there is a linear relationship between relative humidity (RH%), temperature and permeation; as the RH% and temperature increase, so does the rate of oxygen permeability for both PVDC and EVOH film structures.

Table 2-1 Moisture and Temperature Influence on Permeation

Structure	**RH% / Temperature**	**OTR** cm3 x mm/m2 x day x atm
PVDC Saran® 18 film (.019mm)	90% / 40 C	.78 -.48
PVDC Saran® 18 film (.019mm)	10% / 23 C	.18
EVOH	90% / 40 C	.090 - .012
EVOH	10% / 23 C	.01

(Data Source: Permeability Properties of Plastics and Elastomers. Massey, 2003)

It is important to consider these factors when analyzing improvement of oxygen barrier packaging. The shelf-life of a product is determined by the atmosphere in the package and outside the package, depending on how the packaging was processed, filled and the materials used for the packaging structural design. These factors will influence how long the product will survive on the shelf; in this case we're specifically focused on beer and its tendency to oxidize when plastic bottle technologies are incorporated into the primary packaging design. Although the experiments in this research will keep the RH% and temperature constant for all variables, it is necessary to point out these influencing factors that are seen within the environment and how they effect different polymers.

Positioning of Barrier Materials

While the materials are very important in determining permeability along with thickness of materials, the positioning of the barrier material is very important. As Huige points out, high- barrier layers on the outside of the structure tend to have a higher permeation rate than those that are either center layered or that are in the inside of the structure. Opposite to the barrier layer on the outside, the oxygen must first embed itself into the structure —which is slowed down by the initial PET in a multi-layered structure—which in this study is approximately 13mils or .3mm thick for a beer bottle; which then must go through the barrier layering. The outside barrier technologies only have the initial protection that will keep the oxygen away, but will then pass through the remaining plain PET structure. This is the barrier alignment that this particular study will examine.

Crystallinity Effecting Permeation

Crystallinity of the material based on the way the molecular chains are formed through expansion and orientation, also have major effects on the permeability properties of PET in the bottle and film format. The degree of permeation in a polymer structure depends heavily on the packing of the polymer chains and their configurations. The degree to which these chains are aligned can depend on the heating and cooling techniques of the polymer manufacturing process, as well as the particular chemistry of each polymer structure. Highly crystalline or semicrystalline structures like PET form closely knit bonds that are packed tightly due to their aromatic and cyclohexane rings; while semi-crystalline structures such as nylon 6I/6T, polyesters, and butadiene styrene copolymers do not align themselves in a linear pattern; and are more atactic in configuration—yielding an amorphous structure, higher O_2 permeation. Research done by Slee has investigated the properties of amorphous vs. crystalline structures; in particular amorphous regions that contain glycol residue can have more oxygen barrier than those regions that are crystalline. However, generally the more crystalline a structure, the more barrier property it will yield for both moisture and oxygen. Crystallanity involves regular repeating arrangements of molecules and their alignment (Cutler 2004). PVDC because of its melt temperature and composition, has to be produced in such a matter that yields an amorphous structure.

Barrier Film Technologies

There are many oxygen barrier films that perform in the .1-.001 cc•mil/100 in2/24hrs. range: PVOH, EVOH, PVDC, Nylons (polyamides), along with various coatings, treatments, metal deposite, tie layering and laminations. In this particular study, barrier shrink films are used to help break up the steady state of oxygen flow into the bottle wall from the outside. The films used in this study perform differently than other films because they are shrink films, and will tend to have less oxygen barrier.

EVOH (Ethylene vinyl alcohol) is a copolymer that is very hydrophilic due to its OH molecules. This means that it is very attracted to water compared to PE.

PVDC (Polyvinylidene chloride) copolymers are noted for their resistance to both gas and oxygen. Although PVDC can repel both oxygen and water, while EVOH is only oxygen, the oxygen performance of EVOH is much more superior. Because PVDC is very difficult to process because of it's unstable melt range, plasticisers are often added in efforts to bring down the melt range temp. Doing this decreases the crystallinity, while improving processability. However, decreasing the crystallinity of the structure causes an increase in 0_2 permeation.

After reviewing the above literature and general packaging studies it was determined that adding a high barrier shrink film to a plain PET bottle has not been thoroughly documented. Although there is significant research and packaging data on PET beer bottles that are multi-layered and special coated for increasing O_2 barrier, there is no significant reference or studies done on exterior barrier shrink labels or packaging for PET beer bottles in regards to oxygen permeation.

CHAPTER 3: METHODOLOGY

The objective of this thesis research was to prove whether there was any effect of the barrier shrink film added to the plain PET bottle in efforts to reduce and slow down the steady transfer of oxygen permeation. The testing was designed to compare the control plain PET bottle against the same bottle with shrink film. The PET bottle was held as the standard comparison for all other variables. A series of oxygen permeation tests using Mocon's Oxtran 2/21 coulemetric sensor under ASTM D 3985 were run on the all bottle variables. After all shrink wrapped bottles ran the full permeation testing, they were compared to the control.

This chapter describes the methods and equipment used in this thesis research project. It includes descriptions of test specimens, equipment, test parameters, test configuration and protocols.

Material : Plain PET Bottle

The bottles selected for the tests are clear, biaxially orientated .3mm thick, 12oz. Polyethylene terephthalate. Theses bottles are 9" length x 2.5" diameter and are manufactured by Constar Company. These have an average permeation rate of ~ .4 cc/package/day.

Figure 3-1 Plain PET Bottle

Barrier Shrink Film

The Shrink film used in this research were EVOH shrink film , and PVDC shrink film. These particular films used in this research were both from Curwood Company—a division of Bemis. These films are formed from blown extruding shrink lines, that impart shrink characteristics. The PVDC film is made up from PE/tie layer/PVDC/tie layer/PE. The EVOH barrier shrink film is made up of Nylon/tie layer/EVOH/tie layer/PE. The characteristics of these films are described in table 3-1.

Table 3-1 Shrink Films Used in Research Study

Structure	RH% / Temperature	OTR
EVOH Nylon/tie/EVOH/tie/PE (2.0 mils)	0% / 23C	<0.7cc/100in2/24hrs
PVDC PE/tie/PVdC/tie/PE (2.25 mils)	0% / 23C	<1.2cc/100in2/24hrs

The listed OTR's of these particular films are exhibited after shrinking.

Sample Making

All samples were measured out and hand cut for each film specimen. The film was measured out by hand using a straight edge ruler to the exact dimensions in table 3-2. The structures were then cut using scissors against the straight edge to insure that the cuts made were straight and consistent. The bottle was then wrapped in film and placed on the impulse sealer. The impulse sealer was tested with film before the actual samples were made to determine proper dwell and heat settings.

Table 3-2 Film Dimensions used for each Sample

Structure	Length	Width
EVOH (High Barrier Shrink Film)	10.75"	7.25"
PVDC (High Barrier Shrink Film)	10.75"	7.25"

Figure 3-2 Shrink Wrapping Bottles

Shrink Tunnel / Sealing

The shrink tunnel was set at a predetermined speed and heat for all samples to insure the same amount of shrink to the barrier film, however, each type of barrier film will have its own percentage of shrink variance that is unique. Thus before running the tunnel on each substrate for making samples, a test was run on each shrink substrate to ensure that the films properly shrunk to the bottle without distortion. Each film has a different yield at which it begins to thicken up and become more impermeable after exposure to heat. The heat was adjusted accordingly for each sample. The PVDC shrink film was run at 162 ° C using the Damark conveyor shrink tunnel on speed 5. The EVOH shrink film was run @ 145 ° C using the Damark conveyor shrink tunnel on speed 5.

Shrink Procedure

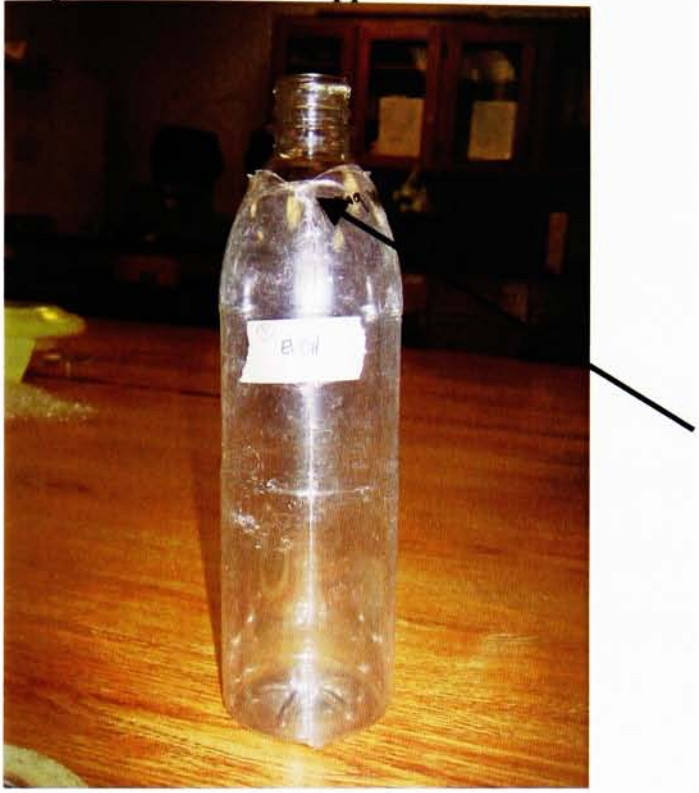
After determining the correct temperature and speed of the tunnel for each varying film, the next step was to develop each specimen. The first step was to fill the plain PET bottle with water to the shoulder of the bottle to prevent the heat of the tunnel from deforming the bottle and shrink film. Then the cap was screwed on the top of the bottle. The pre-cut shrink film pieces were then placed around the bottle. The film was laid down flat on the table and wrapped around the bottle joining the two ends together, forming a center seal line of ¼" in length. The bottom half of the bottle was also sealed off using this method of ¼" length material used for sealing. Using the impulse sealer that is built into the Damark shrink tunnel, the two excess material points (length of the bottle x diameter of the bottom of bottle) were then sealed at a dwell point of 4 and a heat point of 6 on the Damark.

Sample Making Equipment

Figure 3-3 MP Series Damark Shrink Tunnel

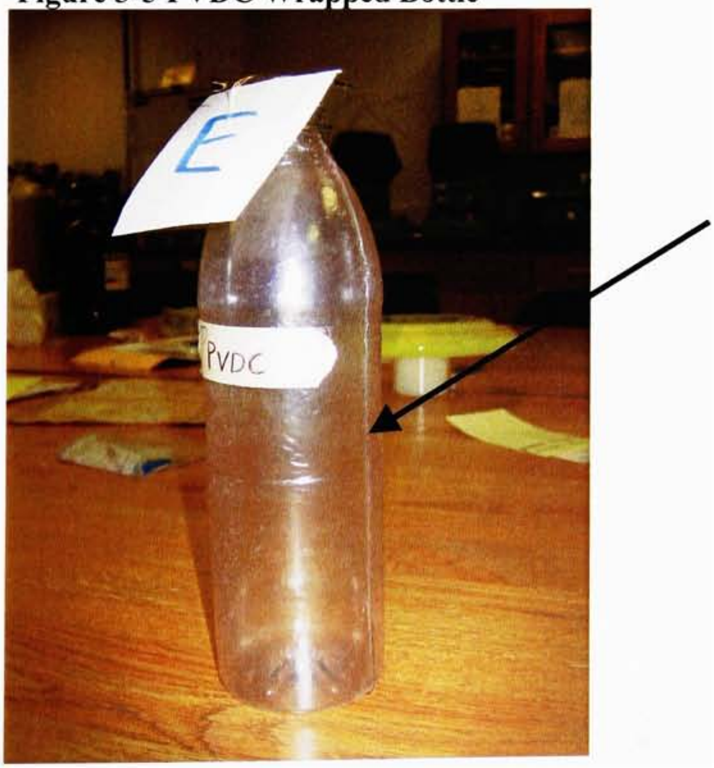
Test Specimens:

Figure 3-4 EVOH Wrapped Bottle



Excess Material after Shrinking

Figure 3-5 PVDC Wrapped Bottle



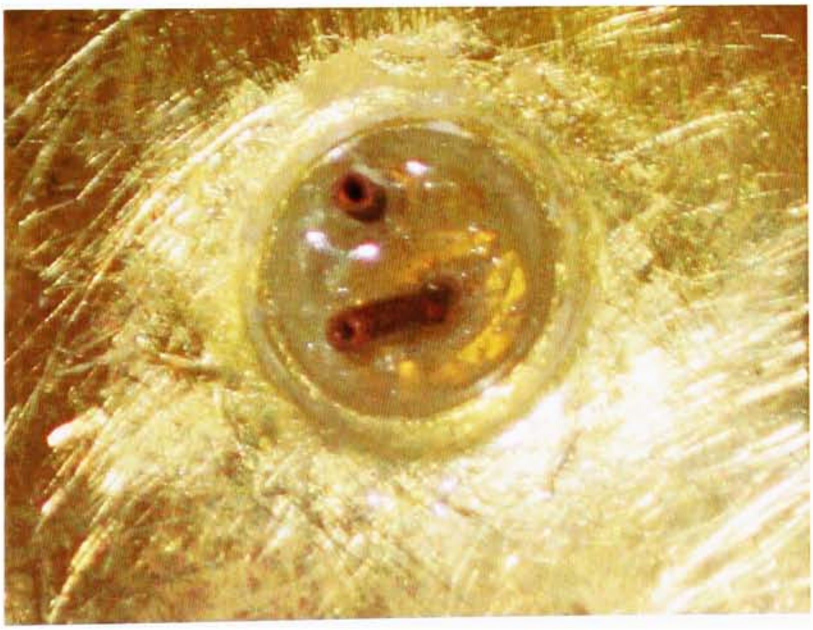
Heat Seal Across Length of Bottle

Bottle Preparation on Fixture:

First step in setting up the bottle and fixture, was to make sure that bottle is dry. Next step was to make sure that the aluminum plate was smooth without any abrasion on the surface that would interfere with the bottle not having flush contact with the plate. But before this, the aluminum plat needed two holes placed in it to run both the carrier gas and receiving tube to the sensor. These copper tubes were fitted and welded into place.

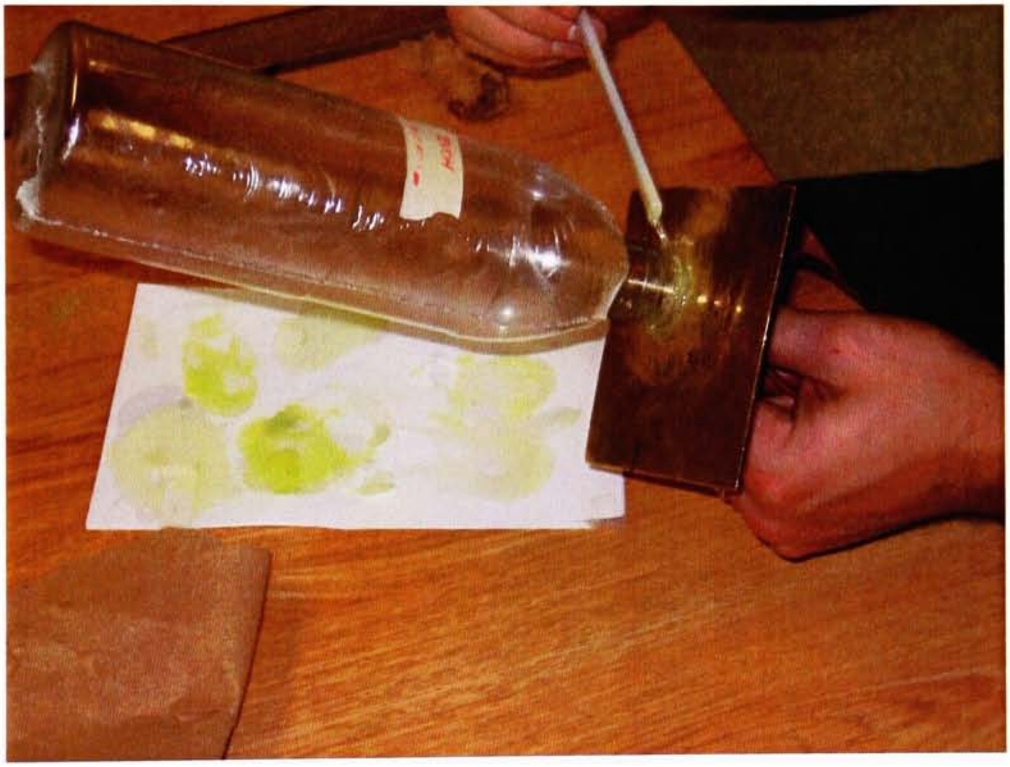
After welding the copper tubing and designing the fixture, the bottle was then used in conjunction with epoxy to create a circular raised epoxy fitting that the bottle could rest on that the tubing went through. This made the task of switching on and off bottles much easier, and the experiment repeatable for continuos sampling.

Figure 3-6 Aluminum Plate with Copper Tubing and Epoxy



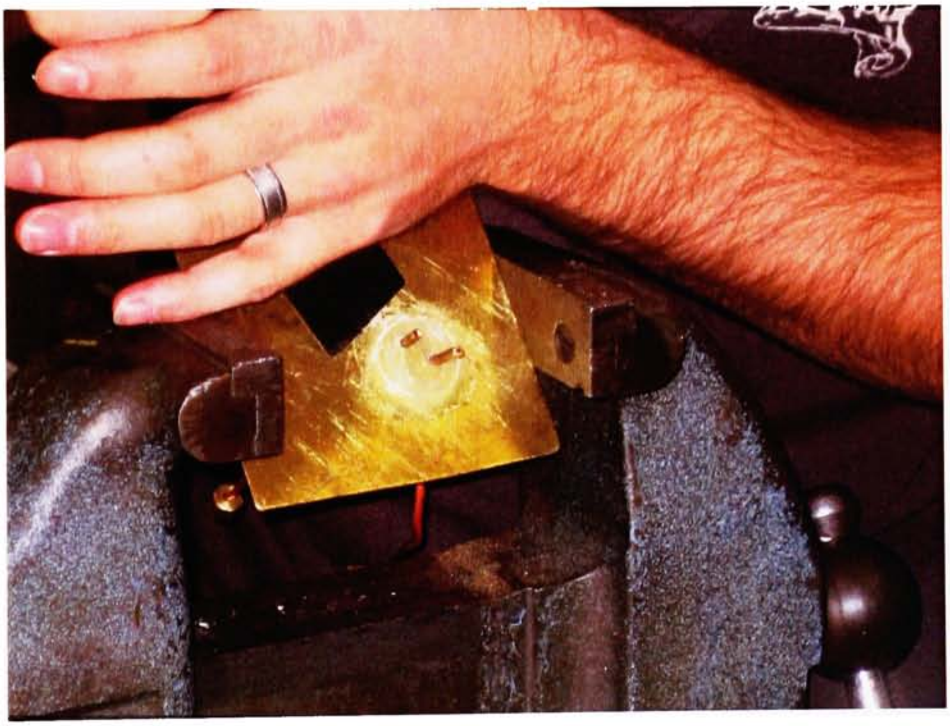
The shrink wrapped bottles where then placed on the plate using epoxy to seal the bottle to the fixture in efforts to hermetically seal them from any outside oxygen ingress. The epoxy was applied to the perimeter of where the top of the closure meets the plate.

Figure 3-7 Applying Epoxy to the Bottle and Plate for Hermetic Seal



Every shrink wrapped bottle that was tested for it's OTR went through this procedure of securing it to the aluminum fixture with epoxy, which was then secured with to the Oxtran 2/21 using a ball fasting seal joint, and brass fittings. As each test was completed, the bottle was taken off the fixture and smoothed once again to run another test.

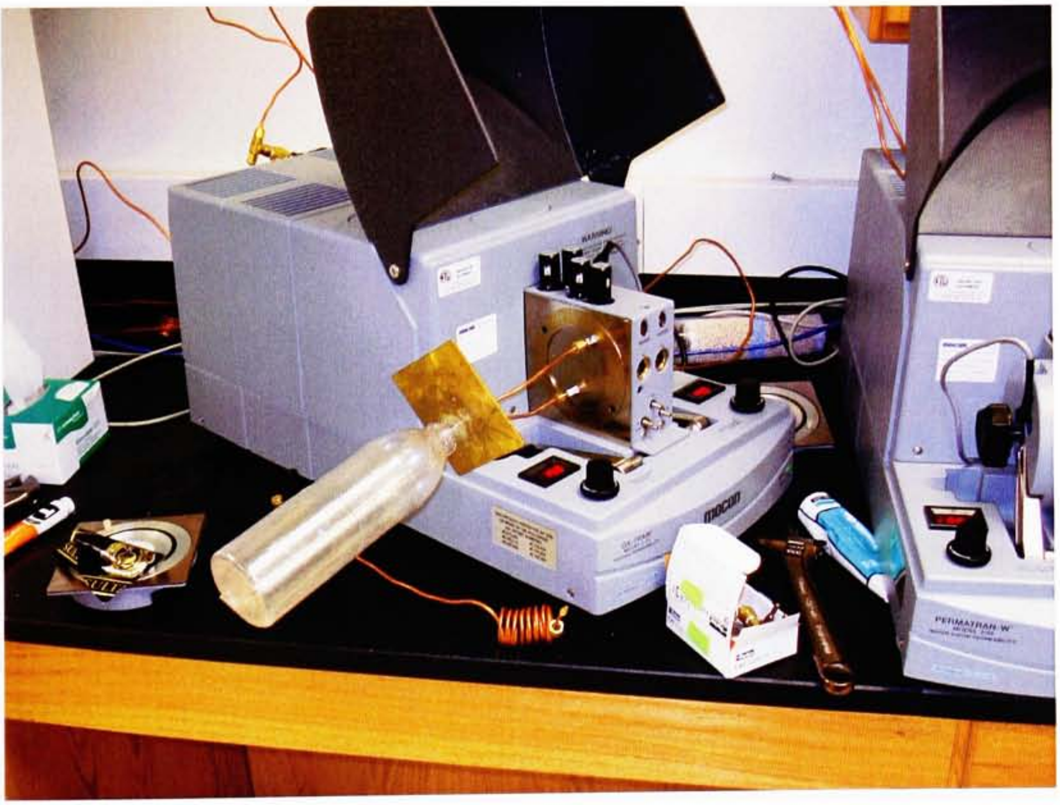
Figure 3-8 Scrapping off Excess Epoxy from Previous Test



Permeation Test Equipment: MOCON OX-TRAN 2/21 HM

Testing consists of oxygen passing over one side of the sample, while nitrogen flows over the other side then out to an oxygen sensative detector. Oxygen permeating through the sample will appear in the nitrogen stream and be measured by the sensor.

Figure 3-9 Mocon Ox-Tran 2/21HM

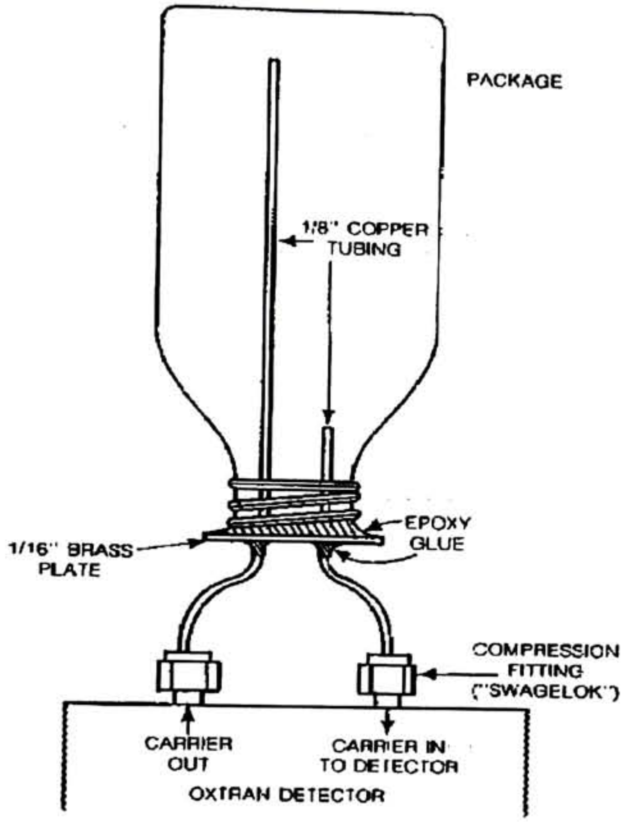


The Oxtran 2/21 ran a purging cycle for 12 hours flushing out all remaining oxygen in the structure along with stabilizing the inside pressure (atm) with the outside of the bottle (IPC Lab). This purge cycle is set to start OTR recording once the structure meets the pressure of the outside atmosphere.

Bottle Fixture: Aluminum Plate and Copper Tubing

Diagram 3-1: Testing Fixture Schematic

Figure 1



The carrier gas (Nitrogen) flows through the bottle continuously from the left copper tube –diagram 3-1. As the nitrogen fills the bottle, it is received by the right copper tube which directly feeds into the coulmetric sensor. The coulmetric sensor detects oxygen that is present in the nitrogen carrier gas. While the nitrogen gas is flowing, the bottle wall is letting in oxygen from the room (21% oxygen in IPC lab), this is how the coulmetric sensor the reads of OTR of each sample. Which it then translates an OTR reading every 30 minutes.

Test Parameters

The test parameters selected as a performance measure in this research was the Oxygen Transmission Rate (OTR) of each individual bottle. The OTR is the measure that indicates how permeable each structure is according to the coulmetric sensor. The OTR reading of each sample determined how much oxygen passes through the bottle wall during the standard 24 hour testing period.

Sample Size

The sample sizes were chosen in efforts to compensate for not having the specimens purge and run the testing in a controlled chamber. For the permeation testing, sample size was determined based on the recommendation of an expert in materials packaging and testing. Because of the limited number of test specimens (ie. PET bottles), the sample size suggested for the test was 20 specimens, however, after experiencing some over-ranging issues with the Oxtran, only 8 data points or specimens were used.

Table 3-3 Specimens Tested

<table>
<tr><td>PVDC/PET</td><td>Plain PET</td><td>PVDC/ PET</td><td>Plain PET</td><td>EVOH/ PET</td><td>Plain PET</td><td>EVOH/ PET</td><td>Plain PET</td></tr>
<tr><td colspan="2">SAMPLE A</td><td colspan="2">SAMPLE B</td><td colspan="2">SAMPLE 1</td><td colspan="2">SAMPLE 2</td></tr>
</table>

Test Protocol: Oxygen Permeation

There was only one kind of test set-up for reading the permeability of the bottles for this project. In this research, the Mocon Oxtran 2/21 HM located in the IPC (Integrated Plastics C Lab) was used to take reading of all bottle structures. The testing was set-up to simulate the oxygen permeation of ambient storage at 23C and 50% RH. The temperature and RH% was chosen based on the lab environment, which wasa help constant throughout all testing.

The standard procedure selected to develop the test protocol was based on ASTM D 3985 and was used to simulate the oxygen permeation in a room's atmospheric condition.

CHAPTER 4: RESULTS, ANALYSIS, AND DISCUSSION

This chapter addresses the test results, analysis, and discussion of the oxygen transmission rates of the test specimens used in this study at their controlled environment.

Oxygen Transmission Rate of Wrapped VS Unwrapped PET Bottles

Table 4-1 A Summary of Actual Data Reading from the Oxtran 2/21 of PDVC Film

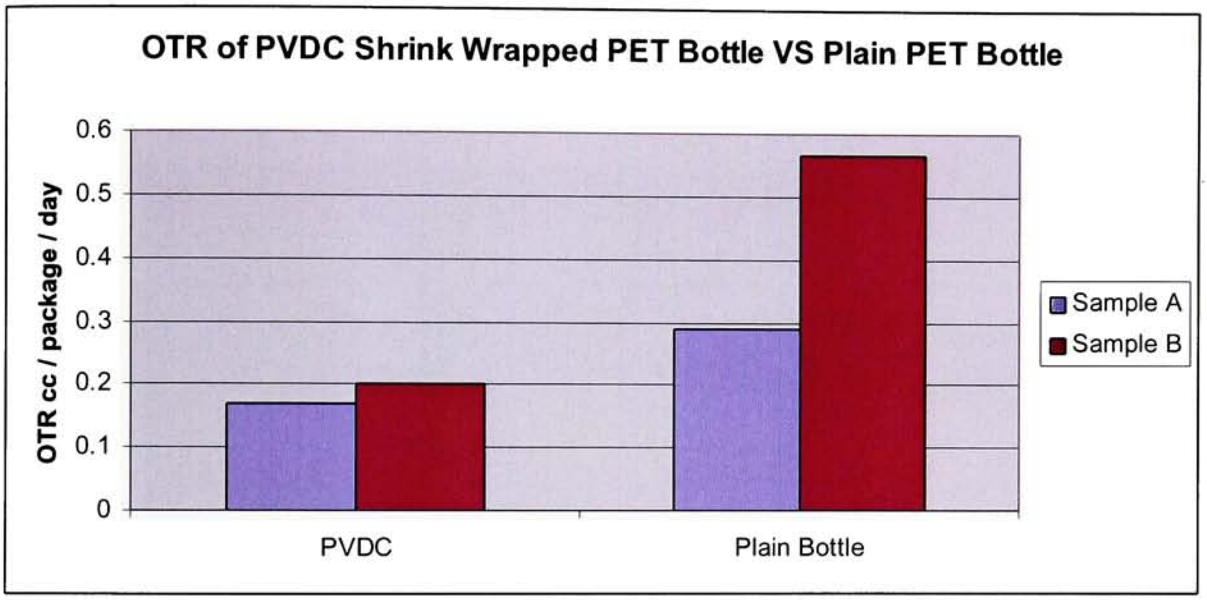


Table 4-2 A Summary of Data Reading from the Oxtran 2/21 of EVOH Film

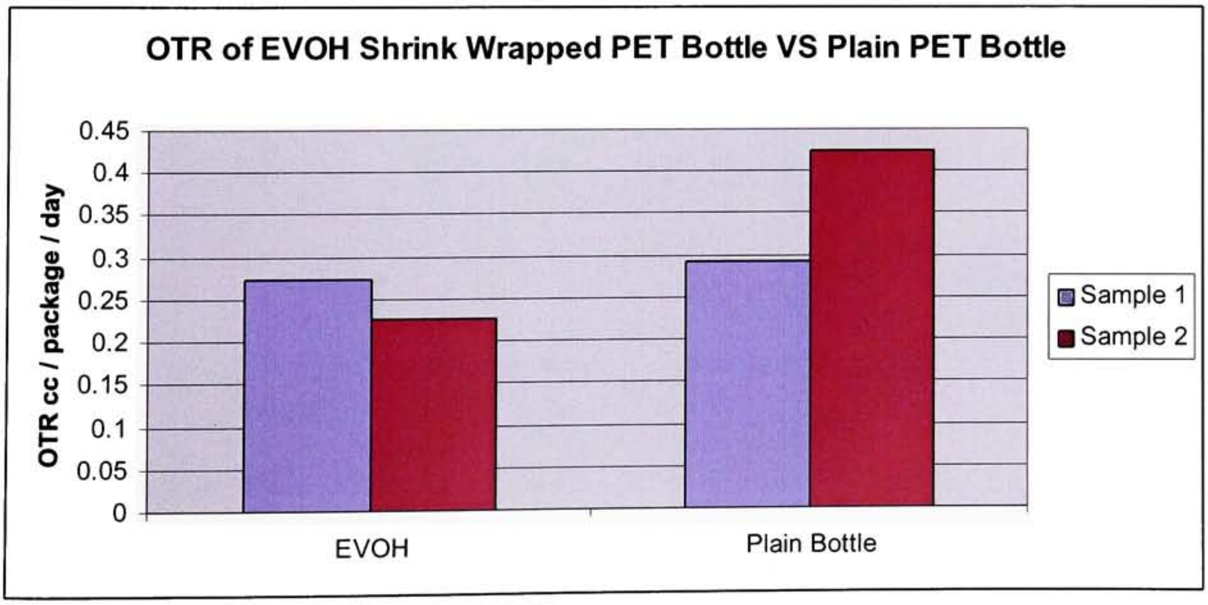


Table 4-1 and 4-2 present the actual data points of oxygen transmission through the bottle wall for both unwrapped and wrapped PET bottles that the Mocon Oxtran 2/21 had collected after each standardized test. These tests were performed at 72 ° F at 50% RH in the IPC Lab.

Table 4-3 A Summary of the Mean Distribution Across Data Points for PVDC Film

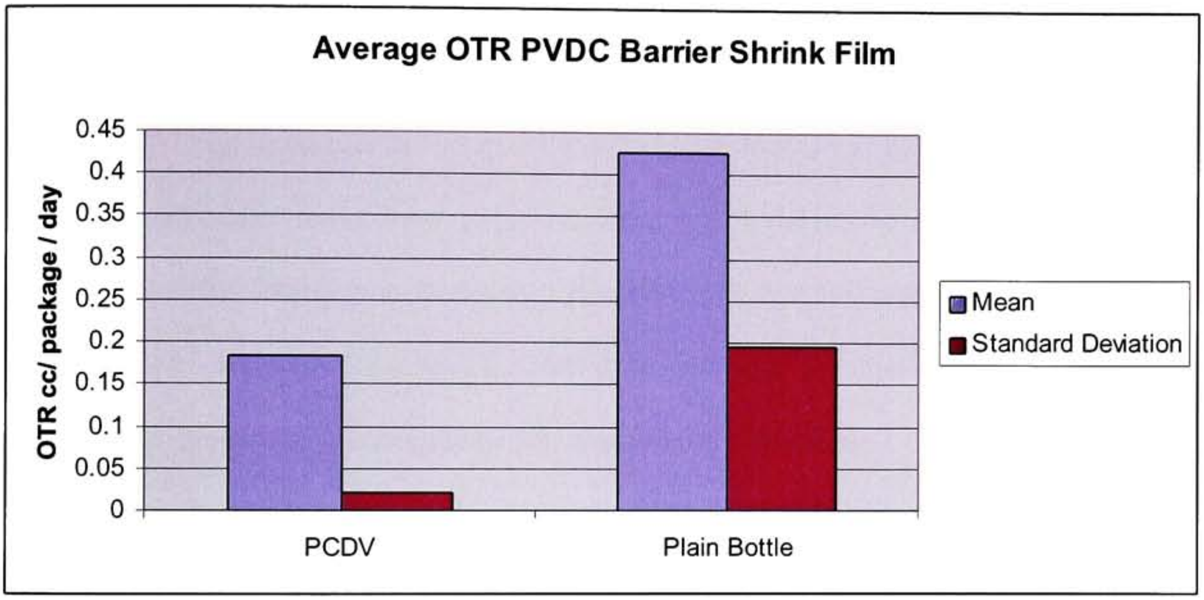
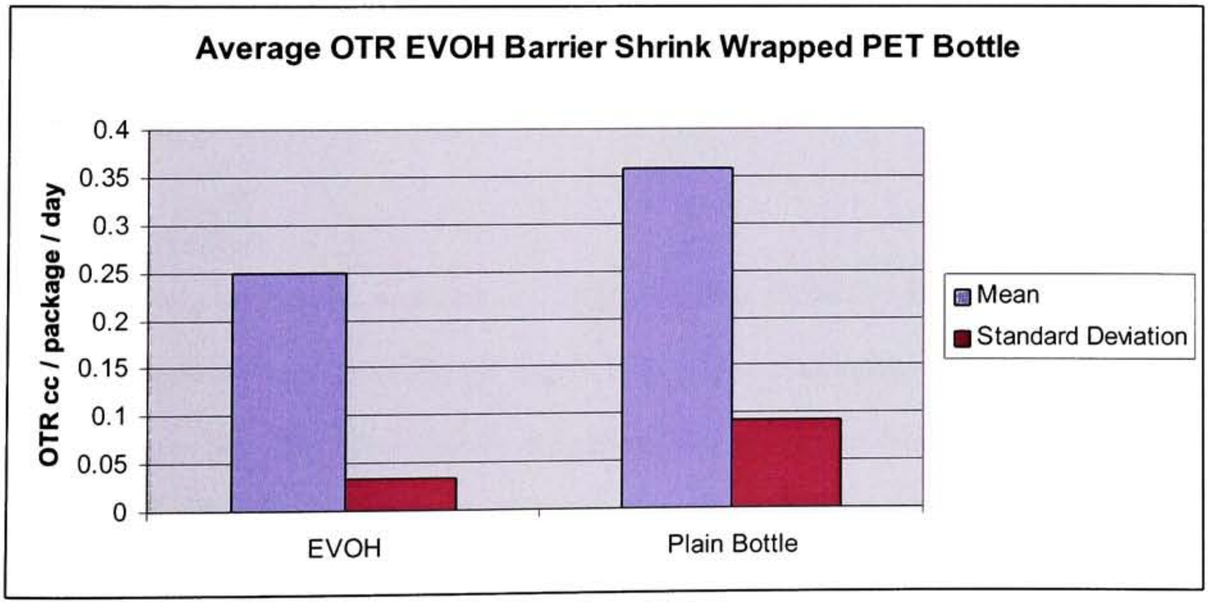


Table 4-4 A Summary of the Mean Distribution Across Data Points for EVOH Film



Tables 4-3 and 4-4 present the mean and standard deviation of both film variants along with mean and standard deviation of the plain PET bottle.

Relationship Between Barrier Film and the Plain PET Bottle

The relationship of the barrier films added to the PET bottles are such that the barrier film helped in reducing the OTR of the bottles for both film variables. Based on the mean data from table 4-3, the PVDC shrink wrapped bottles yielded a decreased OTR from 0.4265575 cc / package/ day (plain PET bottle) to 0.184877 cc / package / day using the PVDC high barrier shrink film. Using the averaged data points, the OTR was reduced by ~ 57%. Based on the mean data from table 4-4, the EVOH shrink wrapped bottles yielded a decreases OTR from 0.3584585 cc / package/ day (plain PET bottle) to 0.250183 cc / package/ day using the EVOH high barrier shrink film.

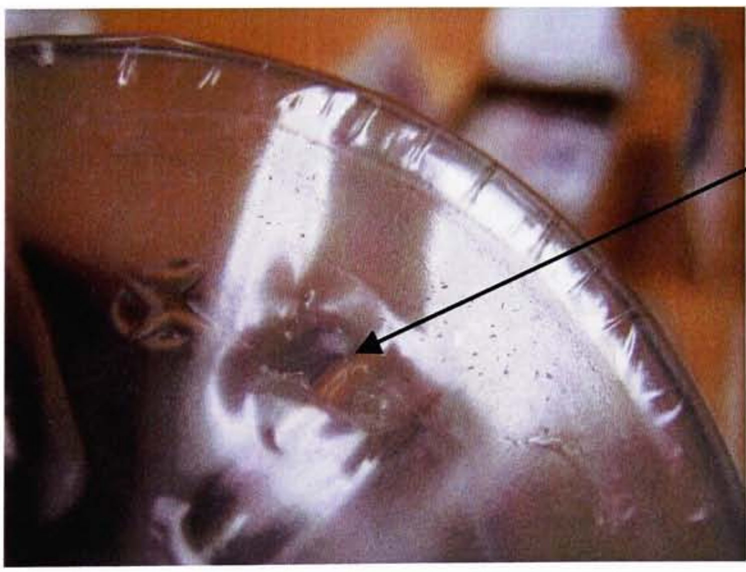
Although the plain PET bottles from both groups of data (PVDC and EVOH) had a wide OTR range, the trend of the plain PET bottle was still showing significant OTR over the film covered bottles. The standard deviation for shrink wrapped data points were much closer to each other than the plain bottles (Appendix- B)

Additional Findings

The original samples that were made that were fully shrink wrapped from the bottom to the neck of the bottle yielded a high OTR. These were in the range of ~.44cc/package/day. The reason for the increase in OTR was due to the sample making process. The samples were not gas flushed, thus the oxygen was trapped in the bottom of each specimen. The oxygen was trapped between the con-caved curvature of the bottom of the bottle, and the oxygen barrier film. This created an air pocket that was acting as a reservoir for air—which was captured during testing. We speculate that the oxygen did not permeate through the bottom of the bottle since this is very thick at ~ 30 mil, but rather collected at the bottom and flowed through the sides to thinner portions of the bottle. The trapped air created pressure that made the oxygen easier to find it's way underneath the barrier shrink film, creating pockets of air that will continue to permeate through the bottle wall as the structure is being tested.

Puncturing the shrink film at the bottom of the bottle to let the oxygen flow freely helped to reduce pressure so that the trapped air was not pushing underneath the barrier film. After doing this there was significant increase in the barrier property of each sample, for both PVDC and EVOH. The trapped air inside the bottom of the bottle was able to move freely and not cause pressure lifting up underneath the bottom edge of the bottle for air to creep in.

Figure 4-1 Puncture in Bottom of Shrink Material



CHAPTER 5: CONCLUSION

Thesis Conclusion

This thesis research was preformed to investigate the effect of oxygen permeability resulting from adding a high barrier shrink film to a PET bottle. The bottles that were chosen for this research were plain biaxially orientated PET, which were then shrink wrapped with high barrier shrink films. There were two different films that were used. EVOH barrier shrink film and PVDC barrier shrink film. To test permeability of these structures, the Mocon Oxtran 2/21 using protocol ASTM D 3985 was used under ambient conditions of 23 ^{o} C at 50% RH.

Although theoretically the EVOH film should have yielded a higher barrier against oxygen permeation, the PVDC film yielded a better barrier over the EVOH by an averaged 28% barrier reduction. Some reasons as to why the PVDC would yield a higher barrier in this research over the EVOH is that the PVDC film was .25 mils thicker than the EVOH film. Also the EVOH film used in this research may have lost some its oxygen barrier capability due to exposure to moisture over time. Both films were kept in the IPC lab that is controlled, but the film could have been exposed to other elements before received at RIT.

Test results demonstrated that there was considerable improvement in oxygen barrier when using both barrier shrink films on the outside of the structure. Although currently used multi-layered and barrier coated PET structures have much higher barrier performance, there was significant improvement when using the outer barrier shrink wraps. The results from this research show that an additional barrier shrink sleeve when applied to the outside of a plain PET will reduce oxygen permeation.

This research will act as the catalyst in spawning the initial idea of barrier shrink film for bottle packaging with quantitative evidence of its success.

Recommendation for Future Research

The examination of the effect of oxygen permeation resulting from adding a high barrier shrink film to a PET beer bottle, was restricted to lab environment temperature and humidity, as well as consistent thickness and surface area of the size of bottle and barrier film. While changes to one of these factors could alter the results of the research, it also creates opportunities for further studies. Recommendations for future research are as follows.

1) As mentioned in the Chapter 2, the effect of OTR is influenced by the temperature and %RH that the materials exhibit while being tested. It would be interesting to observe the same test repeated with higher temperatures and humidity to see how the PET bottle and barrier films would respond

2) Performing the same testing methods and materials as this research but using an environmentally controlled chamber would be an interesting subject.

3) Another variation of this research for further examination would be testing the same film and environmental conditions, but using different amounts of barrier shrink material on each PET bottle—different lengths of the shrink sleeve. This would essentially maintain the idea of using a barrier shrink sleeve rather than using heat sealed film, and testing the OTR at different sleeve lengths. Using pre-cut material that can be slipped over the bottle and put though a heat tunnel would also mire closely simulate industry processes.

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Appendix A

Mocon Oxtran 2/21 OTR Data

PVDC WRAPPED BOTTLE DATA:

Sample A:

========= SECTION NAME: HEADER INFORMATION =========

System Title of Report: MOCON OX-TRAN® 2/21 - Single Test Report for Module Number 1, Cell A

User Supplied Header Information:

Exported on: 10/9/2007 10:03:36 AM

========= SECTION NAME: MODULE 1 INFORMATION =========

Serial Number: MH_01575

Setup Name: Default Setup

Temp Setpoint/Actual: Auto: 23.0 / 23.1 °C.

Barometric Pressure: Manual: 760.00 mmHg

Relative Humidity: Permeant - Man: 0.0%, Carrier - Man: 0.0%

Permeant Concentration: 22 %

Ambient Temp: Manual: 23.0 °C.

========= SECTION NAME: OPERATOR COMMENTS =========

========= SECTION NAME: UNUSUAL LOG ENTRIES =========

========= SECTION NAME: CELL A INFORMATION =========

Test Number: <unspecified>

Material ID: <unspecified>

Using Method: Default Method

Sample Type: pkg: 0.00025 mm

Test Mode: Standard

Control Params: 10 Cycles

ExamMinutes: 30

Individual Zero: No Ind. Zero

Conditioning: Disabled

Cycles Complete: 10

Current Status: Test Done

Started Testing: 10/5/2007 8:03:52 AM

Elapsed Time: 7:30

========= SECTION NAME: TEST RESULTS FOR CELL A =========

IN SELECTED UNITS

Transmission Rate: 0.170255 cc / [pkg - day]

Permeation: 1.6757 E-3 cc - mil / [pkg - day]

========= SECTION NAME: DATA POINTS FROM CELL A =========

Time	Rate / Event
0:00	Test
1:00	0.279723
1:30	0.188813
2:30	0.234920
3:00	0.171507
4:00	0.227728
4:30	0.168791
5:30	0.228237
6:00	0.171856
7:00	0.230780
7:30	0.170255
7:30	Complete

Sample B:

========= SECTION NAME: HEADER INFORMATION =========

System Title of Report: MOCON OX-TRAN® 2/21 - Single Test Report for Module Number 1, Cell A
User Supplied Header Information:
Exported on: 12/10/2007 5:11:34 PM

========= SECTION NAME: MODULE 1 INFORMATION =========

Serial Number: MH_01575
Setup Name: Default Setup
Temp Setpoint/Actual: Auto: 23.0 / 23.1 °C.
Barometric Pressure: Manual: 760.00 mmHg
Relative Humidity: Permeant - Man: 0.0%, Carrier - Man: 0.0%
Permeant Concentration: 22 %
Ambient Temp: Manual: 23.0 °C.

========= SECTION NAME: OPERATOR COMMENTS =========

========= SECTION NAME: UNUSUAL LOG ENTRIES =========

========= SECTION NAME: CELL A INFORMATION =========

Test Number: <unspecified>
Material ID: <unspecified>
Using Method: Default Method
Sample Type: pkg: 0.4 mm
Test Mode: Standard
Control Params: 10 Cycles
ExamMinutes: 30
Individual Zero: No Ind. Zero
Conditioning: 12 Hours
Cycles Complete: 10
Current Status: Test Done
Started Testing: 12/9/2007 9:35:10 PM
Elapsed Time: 19:30

========= SECTION NAME: TEST RESULTS FOR CELL A =========

IN SELECTED UNITS
Transmission Rate: 0.199499 cc / [pkg - day]
Permeation: 3.141720 cc - mil / [pkg - day]

========= SECTION NAME: DATA POINTS FROM CELL A =========

Time	Rate / Event
0:00	Condition
12:00	Test
13:00	0.438162

13:30 0.261010
14:30 0.331244
15:00 0.211665
16:00 0.317558
16:30 0.196581
17:30 0.308522
18:00 0.196352
19:00 0.314034
19:30 0.199499
19:30 Complete

PVDC PLAIN BOTTLE DATA

Sample A:

========= SECTION NAME: HEADER INFORMATION =========

System Title of Report: MOCON OX-TRAN® 2/21 - Single Test Report for Module Number 1, Cell A
User Supplied Header Information:
Exported on: 12/12/2007 11:32:56 AM

========= SECTION NAME: MODULE 1 INFORMATION =========

Serial Number: MH_01575
Setup Name: Default Setup
Temp Setpoint/Actual: Auto: 23.0 / 23.1 °C.
Barometric Pressure: Manual: 760.00 mmHg
Relative Humidity: Permeant - Man: 0.0%, Carrier - Man: 0.0%
Permeant Concentration: 22 %
Ambient Temp: Manual: 23.0 °C.

========= SECTION NAME: OPERATOR COMMENTS =========

========= SECTION NAME: UNUSUAL LOG ENTRIES =========

========= SECTION NAME: CELL A INFORMATION =========

Test Number: <unspecified>
Material ID: <unspecified>
Using Method: Default Method
Sample Type: pkg: 0.3 mm
Test Mode: Standard
Control Params: 10 Cycles
ExamMinutes: 30
Individual Zero: No Ind. Zero
Conditioning: 12 Hours
Cycles Complete: 10
Current Status: Test Done
Started Testing: 12/11/2007 3:08:32 PM
Elapsed Time: 19:30

========= SECTION NAME: TEST RESULTS FOR CELL A =========

IN SELECTED UNITS
Transmission Rate: 0.564856 cc / [pkg - day]
Permeation: 6.671529 cc - mil / [pkg - day]

========= SECTION NAME: DATA POINTS FROM CELL A =========

Time	Rate / Event
0:00	Condition
12:00	Test
13:00	0.697452
13:30	0.589706
14:30	0.633103
15:00	0.560767
16:00	0.630608
16:30	0.561929
17:30	0.630146
18:00	0.561977
19:00	0.629132
19:30	0.564856
19:30	Complete

Sample B:

========= SECTION NAME: HEADER INFORMATION =========

System Title of Report:	MOCON OX-TRAN® 2/21 - Single Test Report for Module Number 1, Cell A
User Supplied Header Information:	
Exported on:	12/10/2007 5:11:34 PM

========= SECTION NAME: MODULE 1 INFORMATION =========

Serial Number:	MH_01575
Setup Name:	Default Setup
Temp Setpoint/Actual:	Auto: 23.0 / 23.1 °C.
Barometric Pressure:	Manual: 760.00 mmHg
Relative Humidity:	Permeant - Man: 0.0%, Carrier - Man: 0.0%
Permeant Concentration:	22 %
Ambient Temp:	Manual: 23.0 °C.

========= SECTION NAME: OPERATOR COMMENTS =========

========= SECTION NAME: UNUSUAL LOG ENTRIES =========

========= SECTION NAME: CELL A INFORMATION =========

Test Number:	<unspecified>
Material ID:	<unspecified>
Using Method:	Default Method
Sample Type:	pkg: 0.4 mm
Test Mode:	Standard
Control Params:	10 Cycles
ExamMinutes:	30
Individual Zero:	No Ind. Zero
Conditioning:	12 Hours
Cycles Complete:	10
Current Status:	Test Done
Started Testing:	12/9/2007 9:35:10 PM
Elapsed Time:	19:30

========= SECTION NAME: TEST RESULTS FOR CELL A =========

	IN SELECTED UNITS
Transmission Rate:	0.199499 cc / [pkg - day]
Permeation:	3.141720 cc - mil / [pkg - day]

========= SECTION NAME: DATA POINTS FROM CELL A =========

Time	Rate / Event
0:00	Condition
12:00	Test
13:00	0.438162
13:30	0.261010
14:30	0.331244
15:00	0.211665
16:00	0.317558
16:30	0.196581
17:30	0.308522
18:00	0.196352
19:00	0.314034
19:30	0.199499
19:30	Complete

Appendix B

OTR DATA POINTS: MEAN & STANDARD DEVIATION

PVDC	Plain Bottle	
0.170255	0.288259	
0.199499	0.564856	
0.184877	0.4265575	**MEAN**
0.02067863	0.1955836	**STDEV**

EVOH	Plain Bottle	
0.274208	0.292917	
0.226157	0.424	
0.2501825	0.3584585	**MEAN**
0.03397719	0.0926897	**STDEV**

Appendix C

PROCESS CONFIGURATION FOR BARRIER SHRINK WRAPPING ON LINE